# Gd-$BiVO_4$ photoanode as catalyst for ciprofloxacin and sulfamethoxazole degradation through solar photoelectrocatalysis

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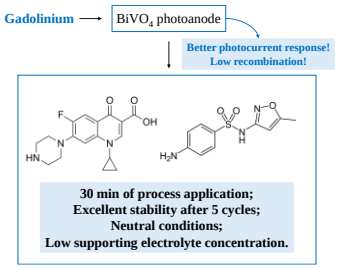
***M. G. Guardiano***[1], *I. M. D. Gonzaga*[1], *L. K. Ribeiro*[1], *L. H. Mascaro*[1]. *(1) Federal University of São Carlos (LIEC-UFSCar), Rodovia Washington Luís, km, 235 - Monjolinho, São Carlos, Brazil, mggds15@gmail.com.*




This study investigated the Gd insertion into $BiVO_4$ photoanode and its influence on physical and photoelectrochemical properties. The photoanode was applied to ciprofloxacin and sulfamethoxazole degradation through solar-photoelectrocatalysis, being analysed the effect of the applied current density and the photoanode reusability. The physical characterization demonstrated a successful Gd insertion, which implied a better photocurrent response and lower semiconductor recombination. Ciporfloxacin (CIP) and sulfamethoxazole (SMX) were almost completely degraded with just 30 min using low current density (1 mA $cm^{-2}$) and supporting electrolyte concentration (0.063 mol $L^{-1}$ NaCl). The photoelectrodes exhibited excellent stability, with negligible degradation observed after 5 cycles, maintaining nearly 100% performance.

## Introduction

Bismuth vanadate ($BiVO_4$) is a semiconductor with good aplications for pharmaceuticals degradation and water splitting by solar-photoelectrocatalysis [1]. However, $BiVO_4$ has a high recombination rate and low stability, thus requiring designer efforts of new materials to optimize stability and reduce electron-hole pair recombination before its application as photoanode [1]. The rare earths doping on $BiVO_4$ can lead to the ion's replacement on the material's crystalline structure and create intermediate energy levels between valence band (BV) and conduction band (BC). It can cause a reduction in recombination and provide stability to the material [2]. This work investigates gadolinium (Gd) insertion into $BiVO_4$ structure and its influence on physical and photoelectronchemical (PEC) properties. The designed photoanode was applied to ciprofloxacin (CIP) and sulfamethoxazole (SMX) degradation by solar photoelectrocatalysis.

## Material and Methods

CIP and SMX stock solutions (100 and 20 mg $L^{-1}$, respectively) were prepared in ultrapure water. $BiVO_4$ and Gd-$BiVO_4$ (5% of gadolinum content) films were produced by $Bi^0$ electrodeposition method [3] on FTO following a 60 μL drop-wise of vanadium (III) acetylacetonate before calcination at 500 ˚C for 2 h. The films were washed for 30 min using NaOH 1 mol $L^{-1}$ for vanadium excess removal after thermal treatment.

The phase composition of the samples were characterized by X-Ray diffraction (XRD, Shimadzu 6000 X-ray Diffraction Protocol) and the morphology of the films was characterized by field emission scanning electron microscopy (SEM-EDS; TM4000 Plus, Hitachi), operating at 15 kV.

The PEC analysis and degradation experiments were performed in a three-electrode cell filled with 0.063 mol $L^{-1}$ NaCl solution (pH 6.8) using $BiVO_4$ and Gd-$BiVO_4$ as working electrode, platinum as counter electrode and Ag/AgCl as reference. The PEC were carried out using a potentiostat/galvanostat (PGSTAT302N, Autolab, Methrom®). The light source was a sun light simulate (Oriel, LCS-100) with 100 mW $cm^{-2}$ of irradiance and the WE exposed area was 1 $cm^2$ from the back side.

## Results and Discussion

The XRD patterns of the $BiVO_4$ and Gd-$BiVO_4$ films (Fig. 1a) demonstrates a monoclinic strucuture (JCPDS 14-0688) with no influence of gadolinum insertion into the $BiVO_4$ active phase, which indicates a succesfully doping with the substitution of bismuth or vanadium. The SEM-EDS images demonstrates a more uniform distribution for Gd-$BiVO_4$ into FTO surface with the presence of Gd on the Gd-BiVO4 film, which is in correspondence with the XRD patterns of the photoanodes (Fig. 1b-c).

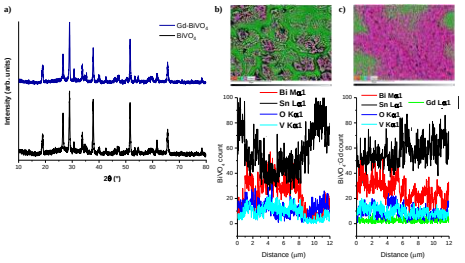



**Fig.1. a)** XDR patterns of $BiVO_4$ and Gd-$BiVO_4$ samples; and SEM-EDS spectra analysis conducted on **b)** $BiVO_4$ and **c)** Gd-$BiVO_4$ surfaces.

PEC measurements indicates that the Gd insertion into $BiVO_4$ film affect its properties (Fig. 2). The Gd insertion was responsible for a current density increase from 170 μA $cm^{-2}$ to 782 μA $cm^{-2}$, when $BiVO_4$ and Gd-$BiVO_4$ films were compared (Fig. 2a), respectively. This insertion also decrease the photoanodes recombination from 52.9% ± 0.2%

using $BiVO_4$ to 32.4% ± 2.1% using Gd-$BiVO_4$. (Fig. 2b). In addition, Gd insertion improve the charge-transfer process, as observed in Nyquist plots in the dark and under solar irradiation (Fig. 2c-d).

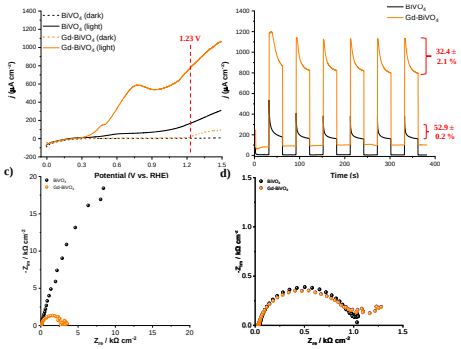



**Fig. 2. a)** Linear voltammetry curves conducted at 5 mV $s^{-1}$; **b)** cronoamperometry on-off appling 1.23 V vs. RHE; and Nyquist diagrams recorded photoanodes in the OER for **c)** dark **d)** light.

CIP and SMX degradation was investigated by solar photoelectrocatalysis under different current densities and through photolysis using NaCl 0.063 mol $L^{-1}$ as supporting electrolyte (Fig. 3). A more lower direct or indirect photolysis of the pharmaceuticals was observed, achieving 53% and 30% of CIP and SMX degradation, respectively, after 30 min. This results indicates that solar irradiation of NaCl solution may can generate $^{\bullet}Cl$ radicals or maybe the pharmaceuticals are susceptible to solar photolysis.

However, the use of the developed photoanode as catalyst resulted in a more faster removal for CIP and SMX antibiotics. Application of 0.5 mA $cm^{-2}$ current density resulted in a complete CIP removal after 15 min and in 99% SMX removal after 30 min of process application. Increase into the applied current density to 1.0 mA $cm^{-2}$ resulted in a complete removal of CIP and SMX after 7.5 and 15 min. In addition, the application of 1.5 mA $cm^{-2}$ implied into complete removal of both antibiotics after 10 min of process application, but with poor photoanode stability and decrease on CIP removal due to instabilities. This result suggests that the optimum value for applied current density to these pharmaceuticals were equal to 1.0 mA $cm^{-2}$. A recent study focused on a real textile wastewater degradation using no modified $BiVO_4$ achieved equal optimum current density to the effluent degradation, which can be associated with the photoanodes stability [4].

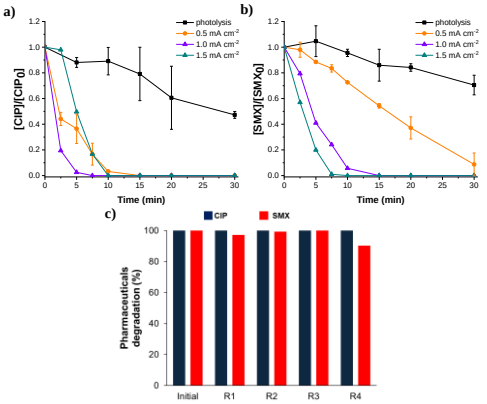



**Fig. 3.** Effect of applied current density on **a)** CIP and **b)** SMX degradation by solar photoelectrocatalysis using Gd-$BiVO_4$ as photoanode; and **c)** Gd-BiVO4 catalyst reuse after 5 cycles. CIP = SMX = 1.0 mg $L^{-1}$; [NaCl] = 0.063 mol $L^{-1}$; pH = 6.8.

Gd-BiVO4 photoanode reuse was investigated to up 5 cycles of solar photoelectrocatalysis process application (Fig. 3c). The obtained results indicates a good photoanode reuse, with complete removal of CIP and SMX degradation decrease to 90% in the 5 cycle of catalyst reuse. These results highlights the importance of Gd insertion into $BiVO_4$ structure to improved the photoanode performance applied to antibiotics degradation.

## Conclusions

In this work a reusable Gd-BiVO4 photoanode was developed and applied to study CIP and SMX antibiotics degradation through solar photoelectrocatalysis. A good pharmaceuticals removal was achieved after 30 min of process application, even after 5 cycles, in neutral conditions and using low supporting electrolyte concentration and low current density (1 mA $cm^{-2}$).


***Acknowledgments***

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